

III.

CHEMICAL AND PHYSICAL PROPERTIES OF ETS

This chapter presents the chemical and physical properties of ETS. Research shows that the combustion of tobacco products leads to the formation of thousands of particulate and gaseous constituents, each with their own physical properties. Among the various tobacco products consumed, cigarettes are the most common and therefore the main contributor to ETS (Jenkins *et al.*, 2000). According to the United States Department of Agriculture, 94 percent of the United States tobacco leaf production was used for cigarettes (USDA, 2001). The discussion below summarizes the research, which has identified the various major components of ETS. The literature cited was produced between 1975 and 2001.

A. ETS AS A COMPLEX MIXTURE

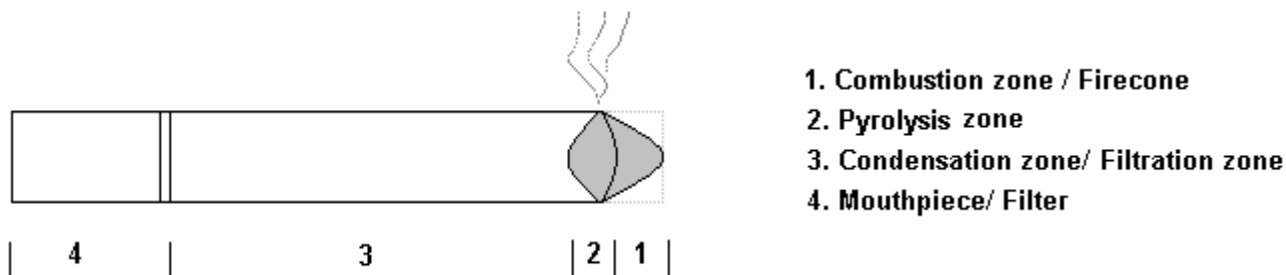
ETS is a complex mixture of thousands of gases and fine particles emitted by the burning of tobacco products and from smoke exhaled by the smoker (NRC, 1986). Other minor contributors are from the smoke that escapes while the smoker inhales and some vapor-phase related compounds that diffuse off the wrapper of the tobacco product. The composition will vary depending on heat of combustion, tobacco content and additives present, and type of filter material used.

Of the thousands of substances that make up ETS, some are formed from combustion and some by atmospheric transformation. Appendix A includes a list of some of the compounds that have been detected in ETS.

Figure III-1 shows a cross section of a cigarette, which helps illustrate the origin of the ETS mixture. Cigarettes are comprised of a tobacco column (region 3), which is housed in a paper, with a filter (region 4) on one end. The combustion firecone (region 1) and pyrolysis zone (region 2) are located at the other end.

Figure III-1

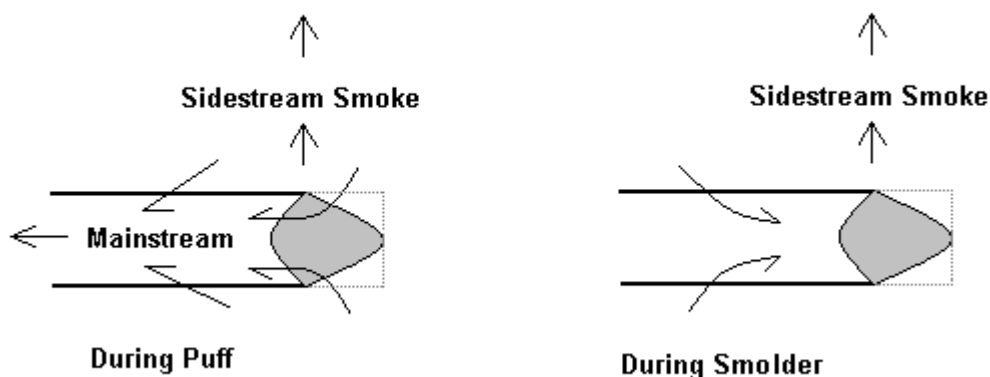
Diagram of a Cigarette



Researchers distinguish cigarette smoke as being comprised of two main components; mainstream and sidestream smoke. Figure III-2 illustrates directions of airflow during smoking. Mainstream smoke is material that is drawn through the mouthpiece of a burning cigarette while sidestream smoke is material that is emitted from a smoldering cigarette between puffs as illustrated in Figure III-2. The OEHHA report *Health Effects of Exposure to Environmental Tobacco Smoke* (OEHHA, 1997) characterizes ETS as a combination of exhaled mainstream smoke, sidestream smoke, and compounds diffused through cigarette paper.

Figure III – 2

Air Flux During Smoking



Ref: Baker, 1980

Similar chemical constituents have been found to be present in both mainstream smoke and sidestream smoke (U.S. EPA, 1992). Differences in constituent quantities are due to variations in burning conditions, such as combustion temperature, differences in pH, and airflow rate. With few exceptions (e.g., hydrogen cyanide and organic acids), sidestream smoke contains greater mass emissions as compared to mainstream smoke (Jenkins *et al.*, 2000) on a per cigarette basis. For example, ammonia emission was measured at 40 to 170 times higher in sidestream smoke than in mainstream smoke (NRC, 1986).

It should also be noted that most crops are treated with pesticides. The U.S. Department of Health and Human Services makes reference to the use of ethylene oxide as a fumigant for tobacco. However, pesticide residues in tobacco are likely to occur only in very low concentrations and be broken down through combustion into smaller non-specific organic chemical components (Fowles and Bates, 2000).

1. Mainstream Smoke

Mainstream smoke is the smoke emitted at the mouthpiece of a burning cigarette. As a person draws in a puff from a cigarette, the airflow creates a lean burning condition with

gas phase temperatures reaching 1562 °F (850 °C) at the core of the firecone and solid phase temperatures reaching 1472 °F (800 °C) at the firecone (Jenkins *et al.*, 2000). At the firecone, core temperatures are high enough to carbonize the tobacco and thus produce an oxygen deficient combustion zone. This region of the firecone contributes to the formation of constituents produced through reductive processes (Jenkins *et al.*, 2000). The gas phase and particulate matter constituents formed are cooled as the air stream passes through the tobacco column and is inhaled through the mouthpiece. The chemistry of the tobacco column changes as combustion products deposit on the remaining tobacco.

2. Sidestream Smoke

Sidestream smoke is emitted from the burning end of a cigarette between puffs and is produced at generally lower temperatures, with a different airflow compared to mainstream smoke (Guerin *et al.*, 1987). The firecone temperatures are lower for sidestream smoke at 1112 °F (600 °C) (Jenkins *et al.*, 2000). Because the smoldering end requires air flow, a vacuum is created in the tobacco column, which acts to drive the flow of air from the filter end through the firecone (Jenkins *et al.*, 2000). Smoldering tobacco with lower temperatures leads to incomplete combustion, which in turn releases more compounds into the sidestream smoke as compared to mainstream smoke per cigarette (NIH, 1998). The result of the U.S. EPA (1992) study on ETS indicates that some compounds are emitted at up to ten times higher in sidestream smoke than in mainstream smoke.

Researchers have correlated the amount of sidestream smoke to the weight of the tobacco and paper consumed during smoldering periods (Jenkins *et al.*, 2000). Studies indicate that sidestream smoke emissions are relatively constant across various cigarette types, including filter, nonfilter, full flavor or low tar cigarettes (U.S. EPA, 1992; Jenkins *et al.*, 2000). Constituents of sidestream smoke are especially subject to phase changes because they are rapidly cooled and extensively diluted with ambient air (Jenkins *et al.*, 2000). Chapter VI contains a more detailed analysis of atmospheric persistence.

B. GAS PHASE COMPONENTS IN ETS

Gas phase constituents are also formed as a result of tobacco combustion. Some of these gas phase constituents are deposited downstream of the burning zone in the tobacco column by filtration and condensation. Those components become part of the fuel for subsequent puffs as the firecone region advances along the tobacco column (Guerin *et al.*, 1987, Jenkins *et al.*, 2000). These processes result in the generation of some chemical constituents found in tobacco smoke that were not originally present in the tobacco plant (Ogden and Jenkins, 1999). Table III-1 shows some of the gas phase constituents, which have been detected in ETS and have known health impacts.

Table III-1

Gas Phase Components in ETS with Known Health Effects

Constituent	TAC^{1/}	Prop 65^{2/}	IARC Class^{3/}	U.S. EPA Class^{4/}
1,3-Butadiene	Yes	Yes		B2
Acetaldehyde	Yes	Yes	2B	B2
Acetone				D
Acetonitrile	Yes			D
Acrolein	Yes		3	C
Benzene	Yes	Yes	1	A
Carbonyl sulfide	Yes			
Ethyl benzene	Yes			D
Formaldehyde	Yes	Yes	2A	B1
Hydrazine	Yes	Yes		
Methanol	Yes			
Methyl chloride	Yes	Yes		D
N-Nitrosodiethylamine		Yes	2A	B2
N-Nitrosodimethylamine	Yes	Yes	2A	B2
N-Nitrosopyrrolidine	Yes	Yes	2B	B2
Styrene	Yes		2B	
Toluene	Yes	Yes		D

NRC, 1986.

Martin *et al.*, 1997.

Notes: ^{1/} Substances identified as Toxic Air Contaminants by California Health and Safety Code section 39655).

^{2/} Chemicals listed under Proposition 65 are known to the State to cause cancer or reproductive toxicity (California Health and Safety Code Section 25249.5 *et seq.*).

^{3/} International Agency for Research on Cancer (IARC) Classification: 1-carcinogenic to humans; 2A-probably carcinogenic to humans with sufficient animal and inadequate or no human evidence; 2B-possible carcinogenic to humans with limited animal and no human evidence; 3-not classifiable as to its carcinogenicity to humans.

^{4/} U.S. EPA classification: A-human carcinogen; B1 probable human carcinogen with sufficient animal and limited human evidence; B2-probable human carcinogen with sufficient animal and inadequate or no human evidence; C-possible human carcinogen; D-not classifiable as to human carcinogenicity.

C. PARTICULATE MATTER COMPONENTS IN ETS

Experimental studies find that cigarette smoke constituents are distributed between the particle phase and gas phase. The proportion of particle to gas components depends on the environmental conditions that affect the individual chemical constituent's volatility and solubility. This proportion may also be affected by conditions at the time of the collection of samples and on the approach used for sampling and analysis. For example, Jenkins *et al.* (2000), measured particle phase constituents, collected on standard Cambridge glass fiber filters, with a particle size of 0.2 µm or larger. In comparison, NRC (1986) measured a particle size 0.1 µm or larger. Basically, in NRC study (1986), the portion of the smoke that passed through a glass-filter fiber that traps all the particles with diameter of 0.1 µm or larger was designated as the gas phase.

Such variability of separation into particulate phase and gas phase reflects specific trapping systems and analytic methods more than prevailing physicochemical conditions of ETS in actual use conditions (NRC, 1986). In general, highly concentrated mainstream smoke has constituents preferentially distributed in the particle phase region (Jenkins *et al.*, 2000). Smaller sidestream smoke particles in the ambient air can be inhaled deeply into the lower respiratory tract, where they can have a deleterious health effect. Table III-2 lists the particulate phase components found in ETS with known health effects.

Table III-2

Constituents of Particulate Matter in ETS with Known Health Effects

Constituent	TAC^{1/}	Prop 65^{2/}	IARC Class^{3/}	U.S. EPA Class^{4/}
2-Naphthylamine		Yes	1	
4-Aminobiphenyl	Yes		1	
Aniline	Yes	Yes	3	B2
Arsenic (inorganic)		Yes	1	A
Benz[a]anthracene	Yes	Yes	2A	B2
Benzo[a]pyrene	Yes	Yes	2A	B2
Cadmium	Yes	Yes	1	B1
Catechol	Yes		2B	
Chromium VI	Yes	Yes	1	A
Dibenzo[a,i]pyrene	Yes	Yes	2B	
Dibenzo[a,l]pyrene	Yes	Yes	2B	
Hydroquinone	Yes		3	
Lead		Yes	2B/3 ^{5/}	B2
N'-Nitrosornicotine		Yes	2B	
Nickel	Yes	Yes	1	A
Nicotine ^{6/}		Yes		
N-Nitrosodiethanolamine			2B	B2
NNK ^{7/}		Yes	2B	
Phenol	Yes		3	D
Quinoline	Yes			B2

NRC 1986.

Notes: ^{1/} Substances identified as Toxic Air Contaminants by Title 17 and 26, California Code of Regulations, Section 93001.

^{2/} Chemicals listed under Proposition 65, known to cause cancer or reproductive toxicity (California Health and Safety Code Section 25249.5 *et seq.*).

^{3/} International Agency for Research on Cancer (IARC) Classification: 1-carcinogenic to humans; 2A-probably carcinogenic to humans; 2B-possible carcinogenic to humans; 3-not classifiable as to its carcinogenicity to humans.

^{4/} U.S. EPA classification: A-human carcinogen; B1 probable human carcinogen with sufficient animal and limited human evidence; B2-probable human carcinogen with sufficient animal and inadequate or no human evidence; C-possible human carcinogen; D-not classifiable as to human carcinogenicity.

^{5/} Inorganic lead – 2B; organolead - 3

^{6/} Also found in gaseous form.

^{7/} NNK: 4-(N-methyl-N-nitrosamino)-1-(3-pyridyl)-1-butanone.

1. ETS Particle Size and Distribution Characterization

ETS particulate is comprised of respirable suspended particles (RSP) (Nelson *et al.*, 1998a). ETS particle size distribution and changes to the distribution with time have been investigated by several researchers under various controlled conditions.

Depending on the environmental conditions and the way cigarettes are consumed, size distribution results vary. Table III-3 shows some notable particle measurement studies by various researchers. Typically, sidestream smoke particles are in the range of 0.01-1.0 μm , while mainstream smoke particles are in the range of size is 0.1-1.0 μm (U.S. EPA, 1992).

Table III-3

ETS Particle Sizes for Various Studies

	Mainstream Smoke	Sidestream Smoke	Reference
Range in particle size	0.1-1.0 μm 0.1-1.0 μm	0.01-0.8 μm 0.01-1.0 μm	Carter and Hasegawa 1975; Hiller <i>et al.</i> , 1982 U.S.EPA, 1992
Particle mean diameter ^{1/}	0.141 μm 0.18 μm 0.41 μm	0.098 μm 0.1 μm 0.32 μm	Nelson <i>et al.</i> , 1998a Guerin <i>et al.</i> , 1987 Carter and Hasegawa 1975, Hiller <i>et al.</i> , 1982
Mass median diameter ^{2/}	0.21 μm	0.185 μm 0.2 μm 0.13 μm 0.16 μm	Nelson <i>et al.</i> , 1998a Ogden and Jenkins, 1999 Morawska <i>et al.</i> , 1997 Ueno and Peters 1986

^{1/} Mean diameter: average of all sizes. ($\mu\text{m} = 10^{-6}$ meter)

^{2/} Mass median diameter: equal number of particles above and below this size. Also referred as Count Median Diameter (CMD).

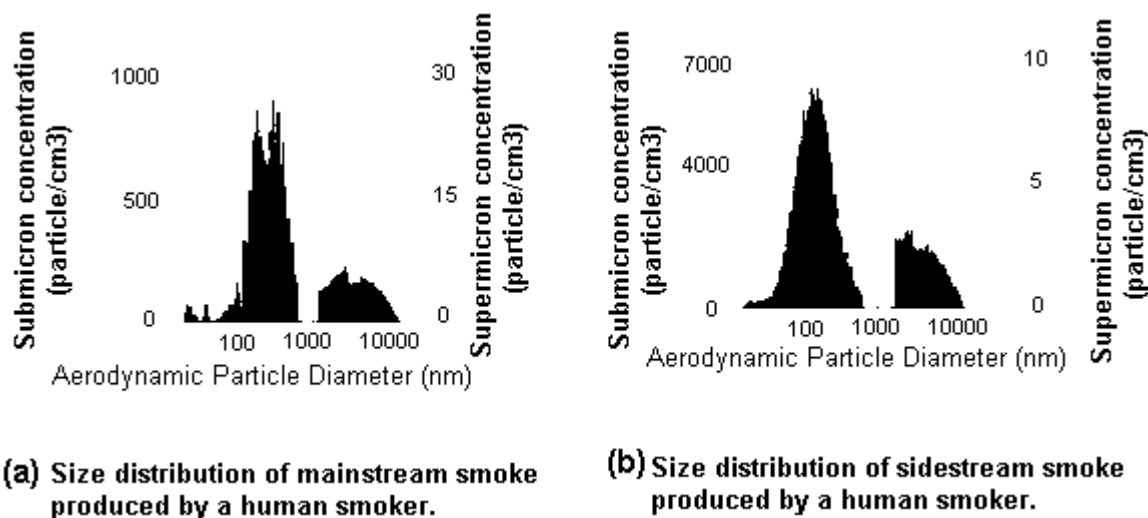
Studies that characterize ETS particles consistently show that sidestream smoke consists of smaller size particles, and are distributed over a broader range of sizes, as compared to mainstream smoke (Ueno and Peters, 1986; Guerin *et al.*, 1987; Carter and Hasagawa, 1975; Hiller *et al.*, 1982; Jenkins *et al.*, 2000).

In a chamber study, Morawska *et al.* (1997), studied a distribution of ETS particles in the range of 0.01 to 30 μm . The Scanning Mobility Particle Sizer (SMPS) and the Aerodynamic Particle Sizer (APS) were used to detect submicron particle level in the range of 0.01 to 0.9 μm and supermicron level in the range of 0.5 to 30 μm , respectively. Figure III-3 shows the results of the study. Morawska *et al.* also found an increase in particle size at a higher humidity level (75 and 95% relative humidity) in the first 30 to 60 minutes after ETS generation. In contrast, a decrease in particle size also has been reported in the literature due to evaporation (Ogden and Jenkins, 1999). Having a broad particle size range, the lifetime of ETS in the air depends strongly on the air exchange rate and other environmental factors. In chamber studies, decreases in

ETS particle concentrations over time were mainly due to ventilation, wall deposition, coagulation, and evaporation of ETS particles (Morawska *et al.*, 1997).

Figure III-3

Size Distribution of ETS Particles



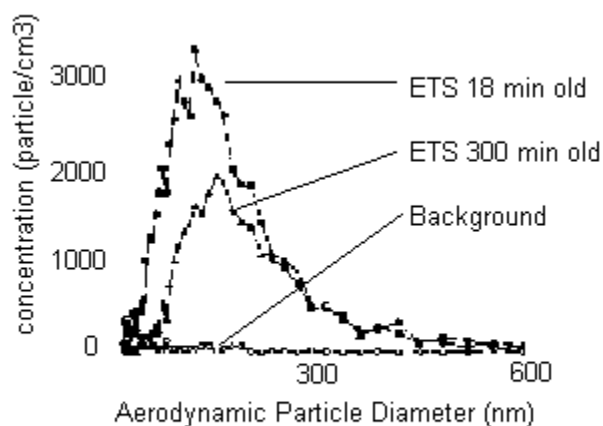
Source: Morawska *et al.*, 1997

The measurements were performed independently by the SMPS(Scanning Mobility Particle Sizer) and the APS (Aerodynamic Particle Sizer) ($\text{nm}=10^{-9}$).

For the Morawska study, Figure III-4 shows the temporal effect on ETS particulate. As shown, ETS concentrations are still well above background levels even at 300 minutes after the initial ETS generation.

Figure III-4

ETS Particle Concentration Over Time



ETS size distribution at the beginning and at the end of the measurement period.

Source: Morawska *et al.*, 1997

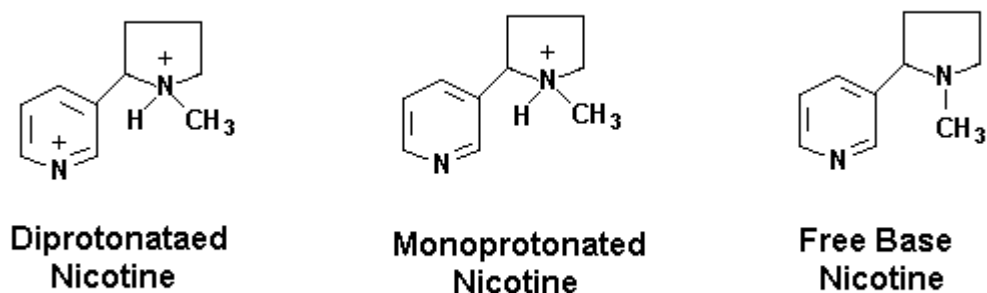
D. NICOTINE (3-(1-METHYL-2-PYRROLIDINYL)-PYRIDINE)

Among the various chemicals found in tobacco, nicotine is a natural constituent and has been found to be the primary cause of chemical addiction. Cigarettes can be viewed as a personal delivery device for a metered dose of nicotine. Airborne nicotine is nearly unique to tobacco smoke in the environment and one of the most common indicators of ETS (Ogden and Jenkins, 1999). Among all surrogates for ETS, nicotine has been used extensively to detect and quantify ETS.

Nicotine is a semi-volatile constituent. Nicotine exists mainly in the particle phase in mainstream smoke but exists primarily in the gas phase in sidestream smoke (Jenkins *et al.*, 2000). Figure III-3 shows forms of nicotine including mono, diprotonated, and free-base nicotine. The diprotonated and monoprotated forms of nicotine are not capable of existing in the gas phase and reside essentially in the particle phase. The free-base form of nicotine can exist in the particle and in the gas phase. Unlike protonated forms of nicotine, the free-base particle form of nicotine can be converted to gas phase nicotine which is then absorbed readily into the blood stream. Ammonia-forming compounds are sometimes added to the tobacco to enhance the generation of gas phase nicotine during smoking. The presence of ammonia raises the possibility of boosting nicotine in the gas phase of the ETS (Pankow *et al.*, 1997). Research has also found that the amount of nicotine in the sidestream smoke is significantly greater than in mainstream smoke (U.K. Department of Health, 2001).

Figure III-3

Three Forms of Nicotine



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